

## PATENT SPECIFICATION

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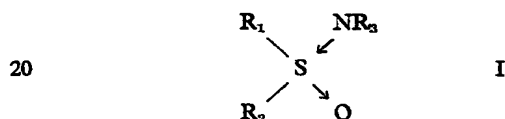


## (54) SULPHOXIMINE DERIVATIVES AND THEIR USE IN HERBICIDAL COMPOSITIONS

- (71) We, SHELL INTERNATIONAL-  
 ALE RESEARCH MAATSCHAPPIJ N.V.,  
 a company organised under the laws of The  
 Netherlands, of 30 Carel van Bylandtlaan,  
 The Hague, The Netherlands, do hereby de-  
 5 clare the invention, for which we pray that a  
 patent may be granted to us, and the method  
 by which it is to be performed, to be particu-  
 10 larly described in and by the following state-  
 ment:—

This invention relates to sulphoximine deri-  
 vatives which exhibit herbicidal and pesticidal  
 properties.

- Accordingly the present invention provides  
 15 biologically active compositions comprising a  
 carrier or a surface-active agent, or both a  
 carrier and a surface-active agent, together  
 with, as active ingredient, at least one sul-  
 phoximine derivative of formula:—



- wherein  $R_1$  represents an optionally sub-  
 stituted aryl group;  $R_2$  represents an alkyl or  
 aryl group or  $R_1$  and  $R_2$  together represent a  
 polymethylene group; and  $R_3$  represents a hy-  
 25 drogen or halogen atom or a nitro or acyl  
 group together with the salts of such deriva-  
 tives. Examples of suitable substituents on the  
 aryl group are halogen atoms and hydroxy,  
 nitro, alkyl, alkyl- and dialkylamino, and di-  
 30 alkylphosphorothionate groups.

The term "acyl" is used herein in its broad-  
 est sense to denote a group obtained by the  
 removal of a hydroxy group from an organic  
 acid and includes not only groups derived from

carboxylic acids and their thio analogues, for  
 example alkanoyl and substituted carbamoyl  
 groups, but also groups derived from sub-  
 stituted carbonic and thiocarbonic acids, for  
 example alkoxy-carbonyl and (alkylthio) car-  
 40 bonyl groups, or from organo sulphur acids, for  
 example an alkyl- or aryl-sulphonyl group.

Preferred compositions are those in which  
 the active ingredient is a sulphoximine deriva-  
 tive of formula I wherein  $R_1$  represents a  
 phenyl group optionally substituted by one or  
 45 more halogen atoms, for example chlorine,  
 bromine or iodine atoms, by one or more nitro  
 groups, or by a hydroxy, alkyl, for example  
 methyl, alkylamino, for example propylamino,  
 dialkylamino, for example dipropylamino, or  
 50 dialkyl phosphorothionate, for example di-  
 ethylphosphorothionate, group;  $R_2$  represents  
 an alkyl group of 1—6 carbon atoms, for ex-  
 ample a methyl or a phenyl group, or  $R_1$  and  
 55  $R_2$  together represent a polymethylene group  
 of up to 5 carbon atoms, for example a tetra-  
 methylene group; and  $R_3$  represents a hydro-  
 gen or chlorine atom, a nitro group, an option-  
 ally chlorinated alkanoyl group of 1—6 car-  
 60 bon atoms, particularly a formyl, acetyl,  
 chloroacetyl, dichloroacetyl, trichloroacetyl,  
 propionyl, dichloropropionyl, butyryl or iso-  
 butyryl group, a cycloalkylcarbonyl group of  
 up to 6 carbon atoms, particularly a cyclo-  
 65 propylcarbonyl group, an aroyl group, particu-  
 larly a benzoyl group, and N - substituted or  
 N,N - disubstituted carbamoyl group, particu-  
 larly a methylcarbamoyl, ethylcarbamoyl,  
 70 phenylcarbamoyl, chlorophenylcarbamoyl, di-  
 chlorophenylcarbamoyl, tolylcarbamoyl or di-  
 methylcarbamoyl group, an alkoxy-carbonyl  
 group, particularly an ethoxy-carbonyl group,  
 an aralkoxy-carbonyl group, particularly a  
 benzyloxy-carbonyl group, an (alkylthio) car-

[Price 25p]

bonyl group, particularly an (ethylthio)-carbonyl group, an alkyl-aryl- or alkarylsulphonyl group, for example a methylsulphonyl, phenylsulphonyl or tosyl group, or a sulphate or alkaryl sulphonate, for example toluene sulphonate, of such a derivative.

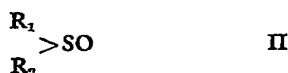
Particularly preferred compositions are those containing, as active ingredient, the compound

10 S - (3,5 - dinitro - 4 - N',N' - dipropylaminophenyl) - S - methylsulphoximine.

The majority of the compounds for use in the compositions of the invention are novel and the invention therefore includes, as novel compounds, sulphoximine derivatives of formula I wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are as defined above in relation to formula I, with the proviso that when R<sub>1</sub> and R<sub>2</sub> each represents a phenyl group or together represent a tetramethylene group, or R<sub>1</sub> represents a phenyl group substituted in the 4-position by chloro, nitro or methyl and R<sub>2</sub> represents a methyl group, then R<sub>3</sub> is other than a hydrogen atom.

25 Subject to this proviso preferred and particularly preferred sulphoximine derivatives are those defined above as active ingredients of the preferred and particularly preferred compositions of the invention.

30 The invention includes also processes for preparing the novel sulphoximine derivatives. Those compounds of Formula I wherein R<sub>3</sub> represents a hydrogen atom are obtained by reacting a sulphoxide of formula:—



35 with hydrazoic acid which may suitably be generated *in situ* by the action of an acid, for example, sulphuric acid, on an alkali metal azide, for example sodium azide. The reaction may be carried out in an organic solvent, for example chloroform.

40 Those compounds wherein R<sub>3</sub> represents an acyl group may in general be obtained by reacting a compound of Formula I wherein R<sub>3</sub> represents a hydrogen atom with an acyl halide, suitably an acyl chloride, preferably in the presence of a hydrogen halide acceptor, for example a tertiary amine, for example triethylamine or pyridine. The reaction may optionally be carried out in an inert organic solvent, for example ether.

50 Alternative processes may be adopted in certain cases and these are sometimes to be preferred as being more convenient. Those compounds wherein R<sub>3</sub> represents an alkanoyl group may be obtained by reacting the appropriate sulphoximine with an acid anhydride, suitably in the presence of the corresponding acid. Those compounds wherein R<sub>3</sub> represents a mono - N - substituted carbamoyl group may be prepared by reacting the sulphoximine with an organic isocyanate.

Those compounds wherein R<sub>3</sub> represents a halogen atom are obtained by the reaction of the sulphoximine with a halogenating agent which may, for example, be the elemental halogen or an alkali metal hypohalite, for example, sodium hypochlorite in acid solution preferably aqueous acetic acid solution. Those compounds wherein R<sub>3</sub> represents a nitro group may be prepared by nitration of the sulphoximine using, for example, a mixture of nitric acid and sulphuric acid.

The term 'carrier' as used herein means a material, which may be inorganic or organic and of synthetic or natural origin, with which the active compound is mixed or formulated to facilitate its application to the plant, seed, soil or other object to be treated, or its storage, transport or handling. The carrier may be a solid or a liquid. Any of the materials usually applied in formulating herbicides and pesticides may be used as carrier.

Suitable solid carriers are natural and synthetic clays and silicates, for example, natural silicas, for example diatomaceous earths; magnesium silicates, for example, talcs; magnesium aluminium silicates, for example, attapulgites and vermiculites; aluminium silicates for example kaolinites, montmorillonites and micas; calcium carbonates; calcium sulphate; synthetic hydrated silicon oxides and synthetic calcium or aluminium silicates; elements, for example, carbon and sulphur; natural and synthetic resins, for example, coumarone resins, polyvinyl chloride and styrene polymers and copolymers; solid polychlorophenols; bitumen; waxes, for example, beeswax, paraffin wax, and chlorinated mineral waxes; and solid fertilisers, for example superphosphates.

Suitable liquid carriers are water, alcohols, for example, isopropanol and glycols; ketones, for example, acetone, methyl ethyl ketone, methyl isobutyl ketone and cyclohexanone; ethers; aromatic hydrocarbons, for example, benzene, toluene and xylene; petroleum fractions, for example, kerosene, light mineral oils; chlorinated hydrocarbons, for example, carbon tetrachloride, perchloroethylene and trichloroethane; and liquefied, normally vaporous, gaseous compounds. Mixtures of different liquids are often suitable.

The surface-active agent may be an emulsifying agent or a dispersing agent or a wetting agent; it may be nonionic or ionic. Any of the surface-active agents usually applied in formulating herbicides or pesticides may be used. Examples of suitable surface-active agents are the sodium or calcium salts of polyacrylic acids and lignin sulphonic acids; the condensation products of fatty acids or aliphatic amines or amides containing at least 12 carbon atoms in the molecule with ethylene oxide and/or propylene oxide; fatty acid esters of glycerol, sorbitan, sucrose or pentaerythritol; condensates of these with ethylene oxide and/or propylene oxide; condensation products of fatty

alcohols or alkyl phenols for example *p*-octylphenol or *p*-octylcresol, with ethylene oxide and/or propylene oxide; sulphates or sulphonates of these condensation products; alkali or alkaline earth metal salts, preferably sodium salts, of sulphuric or sulphonic acid esters containing at least 10 carbon atoms in the molecule, for example, sodium lauryl sulphate, sodium secondary alkyl sulphates, sodium salts of sulphonated castor oil, and sodium alkylaryl sulphonates such as sodium dodecylbenzene sulphonate; and polymers of ethylene oxide and copolymers of ethylene oxide and propylene oxide.

The compositions of the invention may be formulated as wettable powders, dusts, granules, solutions, emulsifiable concentrates, emulsions, suspension concentrates and aerosols. Wettable powders are usually compounded to contain 25, 50 or 75% w of toxicant and usually contain, in addition to solid carrier, 3—10% w of a dispersing agent and, where necessary, 0—10% w of stabiliser(s) and/or other additives, for example penetrants or stickers. Dusts are usually formulated as a dust concentrate having a similar composition to that of a wettable powder but without a dispersant, and are diluted in the field with further solid carrier to give a composition usually containing  $\frac{1}{2}$ —10% w of toxicant. Granules are usually prepared to have a size between 10 and 100 BS mesh; (1.676—0.152mm) and may be manufactured by agglomeration or impregnation techniques.

Generally, granules will contain  $\frac{1}{2}$ —25% w toxicant and 0—10% w of additives, for example stabilisers, slow release modifiers and binding agents. Emulsifiable concentrates usually contain, in addition to the solvent and, when necessary, co-solvent, 10—50% w/v toxicant, 2—20% w/v emulsifiers and 0—20% w/v of appropriate additives, for example stabilisers, penetrants and corrosion inhibitors. Suspension concentrates are compounded so as to obtain a stable, non-sedimenting, flowable product and usually contain 10—75% w toxicant, 0.5—15% w of dispersing agents, 0.1—10% w of suspending agents, for example protective colloids and thixotropic agents, 0—10% w of appropriate additives, for example defoamers, corrosion inhibitors, stabilisers, penetrants and stickers, and as carrier, water or an organic liquid in which the toxicant is substantially insoluble; certain organic solids or inorganic salts may be dissolved in the carrier to assist in preventing sedimentation or as antifreeze agents for water.

The compositions of the invention may contain other ingredients, for example, other compounds possessing herbicidal, pesticidal or fungicidal properties.

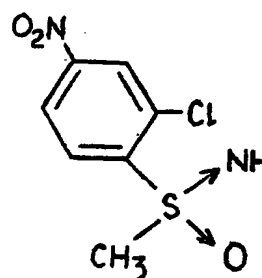
Aqueous dispersion and emulsions, for example, compositions obtained by diluting a wettable powder or an emulsifiable concentrate

according to the invention with water, also lie within the scope of the present invention. The said emulsions may be of the water-in-oil or of the oil-in-water type, and may have a thick 'mayonnaise'-like consistency.

The invention includes also within its scope a method of combating weeds and/or insects and/or acarids at a locus which comprises applying to the locus a biocidally effective amount of a composition or sulfoximine derivative of the invention.

The invention is illustrated further in the following Examples.

Example 1.  
S - (2 - chloro - 4 - nitrophenyl) - S - methylsulphoximine



2 - Chloro - 4 - nitrophenyl - methylsulphoxide (11 g) was dissolved in a mixture of dry chloroform (200 ml) and concentrated sulphuric acid (20 ml). Dry sodium azide (6.5 g) was added to the mixture maintained at 48—53° C. over a period of three hours. The mixture was stirred vigorously for a further 24 hours at this temperature, and then poured into ice-water. The chloroform layer was separated and the aqueous layer neutralised with aqueous sodium carbonate solution. The neutralised solution was extracted with chloroform and the combined chloroform solutions were dried over anhydrous sodium sulphate and evaporated to dryness under reduced pressure to yield the desired product having a m.p. 85—88° C.

Analysis

Calculated for  $C_7H_7N_2SO_3Cl$ :

C 35.9; H 3.0; N 11.9%

Found: C 36.2; H 2.9; N 11.9%

Example 2  
S - (2 - chloro - 4 - nitrophenyl) - S - methyl-N - acetylsulphoximine

S - (2 - chloro - 4 - nitrophenyl) - S - methylsulphoximine (1.5 g, prepared as in Example 1) and acetic anhydride (1 ml) in glacial acetic acid (4 ml) were heated together at 50° C. for 1 hour. Water was then added to the mixture and the resulting solid was filtered off, dried and recrystallised from a mixture of

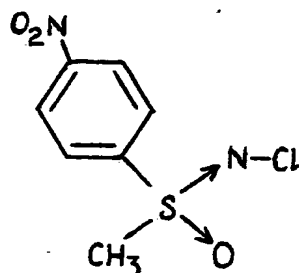
acetone and petroleum ether (b.p. 40—60° C.) to give the desired product having a m.p. 161—163° C.

#### Analysis

- 5     Calculated for  $C_7H_7N_2SO_3Cl$ :  
           C 39.2; H 3.3; N 10.1; S 11.6%  
       Found: C 39.7; H 3.3; N 10.3; S 11.6%

#### Example 3

- 10    S - methyl - S - (4 - nitrophenyl) - N - chlorosulphoximine



- 15    S - methyl - S - (4 - nitrophenyl) sulphoximine (1.0 g) in dry chloroform (50 ml) was treated with gaseous chlorine under irradiation by a heat lamp for 2 hours. The mixture was then filtered and resulting solid was recrystallised from a mixture of acetone and petroleum ether (b.p. 40—60° C.) to yield the desired product having a m.p. 158—160° C.

#### Analysis

- 20     Calculated for  $C_7H_7N_2SO_3Cl$ :  
           C 35.9; H 3.0; N 12.0; S 13.7%  
       Found: C 35.7; H 3.7; N 11.7; S 13.4%

#### Example 4

- 25    S - methyl - S - (4 - nitrophenyl) - N - (N',N' - dimethylcarbamoyl) sulphoximine  
       S - methyl - S - (4 - nitrophenyl) sulphoximine (0.75 g) and dimethylcarbamoyl chloride (0.4 g) in dry pyridine (40 ml) were heated together under reflux for 6 hours. The solution was then evaporated to dryness under reduced pressure. The residue was treated with dilute hydrochloric acid and extracted with benzene. The benzene extracts were dried and evaporated to dryness under reduced pressure to yield the desired product having a m.p. 135—137° C.

#### Analysis

- 40     Calculated for  $C_{10}H_{13}N_3SO_3$ :  
           C 44.4; H 4.8; S 11.8%  
       Found: C 44.3; H 4.7; S 12.4%

#### Example 5

- 45    S - methyl - S - (4 - nitrophenyl) - N - (N' - phenylcarbamoyl) sulphoximine  
       S - methyl - S - (4 - nitrophenyl) sul-

phoximine (1.0 g) and phenyl isocyanate (0.6 g) in a 2:1 mixture of toluene and petroleum ether (b.p. 60—80° C.) were heated together under reflux for 4½ hours. The solution was filtered and evaporated to dryness under reduced pressure. The residue was triturated with a hot mixture of acetone and petroleum ether (b.p. 60—80° C.) to give the desired product as a crystalline solid having a m.p. 148—150° C.

#### Analysis

- 55     Calculated for  $C_{13}H_{13}N_3SO_3$ :  
           C 52.7; H 4.1; N 13.3%  
       Found: C 53.0; H 4.2; N 13.0%

#### Example 6

- 60    S - (4 - chlorophenyl) - S - methyl - N - ethoxycarbonylsulphoximine  
       S - (4 - chlorophenyl) - S - methylsulphoximine (0.76 g), ethyl chloroformate (0.43 g) and triethylamine (0.4 g) in ether (40 ml) were heated together under reflux for 6½ hours. The mixture was then filtered and evaporated to dryness under reduced pressure to give the desired product having a m.p. 70—73° C.

#### Analysis

- 70     Calculated for  $C_{10}H_{12}N_2SO_3Cl$ :  
           C 45.9; H 4.6; N 5.4%  
       Found: C 45.9; H 4.8; N 5.2%

#### Example 7

- 75    Nitration of S - (4 - chlorophenyl) - S - methylsulphoximine  
       S - (4 - chlorophenyl) - S - methylsulphoximine (1.0 g) was treated dropwise with fuming sulphuric acid (3 ml) followed by fuming nitric acid (1 ml) at 5—15° C. The mixture was stirred at 30—35° C. for 6 hours and then poured into ice-sodium hydroxide solution. After vigorous stirring a white precipitate was obtained, which was filtered off, dried and recrystallised from a mixture of acetone and petroleum ether (b.p. 40—60° C.) to yield S - (4 - chloro - 3 - nitrophenyl) - S - methyl - N - nitrosulphoximine as a colourless crystalline solid having a m.p. 164—168° C.

#### Analysis

- 90     Calculated for  $C_7H_6N_2SO_3Cl$ :  
           C 30.1; H 2.2; N 15.0; S 11.5%  
       Found: C 30.4; H 2.0; N 14.8; S 11.6%

The aqueous alkaline solution was acidified and extracted with chloroform. The extracts were dried and evaporated to dryness under reduced pressure to yield a crude material which after recrystallisation from benzene yielded S - (4 - chloro - 3 - nitrophenyl) - S - methylsulphoximine having a m.p. 118—120° C.

#### Analysis

- 100    Calculated for  $C_7H_7N_2SO_3Cl$ :  
           C 35.8; H 3.0; N 11.9%  
       Found: C 36.1; H 3.0; N 11.3%  
       105

- Example 8  
S - (4 - chlorophenyl) - S - methyl - N - tosylsulphoximine  
S - (4 - chlorophenyl) - S - methylsulphoximine (1.89 g) and *p* - toluenesulphonyl chloride (1.90 g) in pyridine (10 ml) were heated together at 100° C. for 3 hours. Water was added to the cooled solution to precipitate a crude product which on recrystallisation from ethanol gave the desired product having a m.p. 125—127° C.
- Example 9  
Following procedures similar to those given in the preceding Examples further compounds were prepared, whose physical characteristics and analysis are set out in Table 1.

TABLE 1

Compound	Melting Point °C.	Analysis
S-(4-chlorophenyl)-S-methyl-N-acetyl-sulphoximine	75—80	Calculated for $C_9H_{10}NSO_2Cl$ : C 46.7; H 4.4; N 6.0% Found : C 46.6; H 4.4; N 5.8%
S-methyl-S-(4-nitrophenyl)-N-acetyl-sulphoximine	119—121	Calculated for $C_9H_9N_2SO_4$ : C 45.7; H 4.1; N 11.6; S 13.2% Found : C 45.3; H 4.3; N 11.5; S 13.1%
S-(4-chloro-2-nitrophenyl)-S-methyl-sulphoximine	114—116	Calculated for $C_7H_7N_2SO_3Cl$ : C 35.9; H 3.0; N 11.9% Found : C 36.1; H 2.9; N 10.5%
S-(3,5-dinitro-4-N',N'-dipropylaminophenyl)-S-methylsulphoximine	85—88	Calculated for $C_{13}H_{16}N_4SO_3$ : C 45.4; H 5.9; N 16.3% Found : C 45.1; H 5.9; N 16.3%
S-methyl-S-(2-nitrophenyl)sulphoximine	94—96	Calculated for $C_7H_9N_2SO_3$ : C 42.1; H 4.0; N 14.0% Found : C 42.4; H 4.3; N 13.6%
S-methyl-S-(4-nitrophenyl)-N-(N'-methyl carbamoyl)sulphoximine	131—133	Calculated for $C_9H_{11}N_3SO_4$ : C 42.0; H 4.3% Found : C 41.7; H 4.3%
S-methyl-S-(4-nitrophenyl)-N-(N'-(3-chlorophenyl)carbamoyl)sulphoximine	154—156	Calculated for $C_{14}H_{13}N_3SO_4Cl$ : C 47.5; H 3.4; N 11.9; S 9.0% Found : C 47.4; H 3.4; N 11.6; S 9.2%
S-(2-chloro-4-nitrophenyl)-S-methyl-N-(N'phenylcarbamoyl)sulphoximine	219—222	Calculated for $C_{14}H_{12}N_3SO_4Cl$ : C 47.5; H 3.4; N 11.9; S 9.0% Found : C 49.4; H 3.8; N 11.4; S 9.3%

TABLE 1 (Continued)

Compound	Melting Point °C.	Analysis
S-(2-chloro-4-nitrophenyl)-S-methyl-N-(N'-(3-chlorophenyl)carbamoyl)sulphoximine	168—170	Calculated for $C_{14}H_{11}N_3SO_4Cl_2$ : C 43.3; H 2.8; N 10.8% Found : C 43.5; H 3.0; N 10.6%
S-(4-chlorophenyl)-S-methyl-N-(N'-phenylcarbamoyl)sulphoximine	149—151	Calculated for $C_{14}H_{13}N_3SO_2Cl$ : C 54.4; H 4.2; N 9.1% Found : C 54.6; H 4.3; N 9.0%
S-(4-chlorophenyl)-S-methyl-N-(N'-(3-chlorophenyl)carbamoyl)sulphoximine	131—134	Calculated for $C_{14}H_{11}N_3SO_2Cl_2$ : C 49.0; H 3.5; N 8.2; S 9.3% Found : C 48.7; H 3.4; N 8.3; S 9.5%
S-methyl-S-p-tolyl-N-(N'-(3,4-dichlorophenyl)carbamoyl)sulphoximine	182—184	Calculated for $C_{15}H_{14}N_3SO_2Cl_2$ : C 50.5; H 3.9; N 7.8% Found : C 50.3; H 4.1; N 7.8%
S-methyl-S-(4-nitrophenyl)-N-(N'-(3,4-dichlorophenyl)carbamoyl)sulphoximine	127—129	Calculated for $C_{14}H_{11}N_3SO_4Cl_2$ : C 43.3; H 2.8; N 10.8% Found : C 44.6; H 3.0; N 10.6%
S-(4-chlorophenyl)-S-methyl-N-((ethylthio)carbonyl)sulphoximine	88—90	Calculated for $C_{10}H_{12}N_2SO_2Cl$ : C 43.2; H 4.3; N 5.0% Found : C 43.6; H 4.6; N 5.0%
S-methyl-S-(4-nitrophenyl)-N-(N'-ethylcarbamoyl)sulphoximine	105—107	Calculated for $C_{11}H_{13}N_3SO_4$ : C 44.3; H 4.8; N 15.5% Found : C 44.3; H 5.0; N 15.2%
S-(4-chloro-3-nitrophenyl)-S-methyl-N-(N'-methylcarbamoyl)sulphoximine	169—171	Calculated for $C_{10}H_{10}N_3SO_4Cl$ : C 37.1; H 3.4; N 14.4; S 11.0% Found : C 39.1; H 3.6; N 13.6; S 10.6%
S,S di - phenyl - N - (N' - methylcarbamoyl)-sulphoximine	183—185	Calculated for $C_{11}H_{11}N_3O_2$ : C 61.4; H 5.2; N 10.2% Found : C 61.5; H 5.1; N 11.6%
S-(3,5-dinitro-4-propylaminophenyl)-S-methylsulphoximine	160—162	Calculated for $C_{10}H_{14}N_4SO_6$ : C 39.8; H 4.6; N 18.6; S 10.6% Found : C 40.1; H 4.7; N 18.1; S 10.5%

TABLE I (Continued)

Compound	Melting Point °C.	Analysis
S-(3,5-dinitro-4-N,N'-dipropylaminophenyl)-S-methyl-N-acetylsulphoximine	160—162	Calculated for $C_{16}H_{22}N_4SO_6$ : C 46.6; H 5.7; N 14.5% Found : C 46.4; H 5.8; N 14.2%
S-(3,5-dinitro-4-N,N'-dipropylaminophenyl)-S-methyl-N-methanesulphonylsulphoximine	189—191	Calculated for $C_{14}H_{22}N_4S_2O_7$ : C 39.8; H 5.2; N 13.3% Found : C 40.0; H 5.5; N 13.2%
S-(3,5-dinitro-4-N,N'-dipropylaminophenyl)-S-methyl-N-tolylsulphoximine	182—184	Calculated for $C_{20}H_{26}N_4S_2O_7$ : C 48.1; H 5.3; N 11.2% Found : C 47.8; H 5.5; N 11.2%
S-(3,5-dinitro-4-N,N'-dipropylaminophenyl)-S-methyl-N-(N'-phenylcarbamoyl)sulphoximine	194—195	Calculated for $C_{20}H_{26}N_5SO_6$ : C 51.8; H 5.4; N 15.1% Found : C 51.4; H 5.5; N 14.8%
S,S-tetramethylene-N-(N'- <i>m</i> -tolylcarbamoyl)sulphoximine	128—130	Calculated for $C_{12}H_{18}N_2SO_2$ : C 57.2; H 6.4; N 11.1% Found : C 57.1; H 6.3; N 10.8%
S,S-tetramethylene-N-(benzyloxycarbonyl)sulphoximine	80—82	Calculated for $C_{12}H_{16}N_2SO_3$ : C 56.9; H 6.0; N 5.5; S 12.7% Found : C 57.3; H 6.2; N 5.4; S 13.1%
S-(3,5-dinitro-4-N,N'-dipropylaminophenyl)-S-methyl-N-(N'-methylcarbamoyl)sulphoximine	145—147	Calculated for $C_{16}H_{22}N_4SO_6$ : C 45.0; H 5.8; N 17.5% Found : C 45.1; H 5.8; N 17.2%
S-(3,5-dinitro-4-N,N'-dipropylaminophenyl)-S-methyl-N-chloroacetylsulphoximine	180—182	Calculated for $C_{15}H_{21}N_4SO_6Cl$ : C 42.8; H 5.0; N 13.3; S 7.6% Found : C 42.9; H 5.1; N 12.9; S 7.8%
S-(3,5-dinitro-4-N,N'-dipropylaminophenyl)-S-methyl-N-dichloroacetylsulphoximine	213—215	Calculated for $C_{15}H_{20}N_4SO_6Cl_2$ : C 39.6; H 4.4; N 12.3; S 7.0% Found : C 39.9; H 4.4; N 12.2; S 7.2%
S-(3,5-dinitro-4-N,N'-dipropylaminophenyl)-S-methyl-N-trichloroacetylsulphoximine	236—237	Calculated for $C_{15}H_{19}N_4SO_6Cl_3$ : C 36.8; H 3.9; N 11.4% Found : C 37.2; H 4.0; N 11.2%
S-(3,5-dinitro-4-N,N'-dipropylaminophenyl)-S-methyl-N-cyclopropylcarbonylsulphoximine	184—186	Calculated for $C_{17}H_{24}N_4SO_6$ : C 49.4; H 5.9; N 13.6% Found : C 49.2; H 6.1; N 13.2%
S-methyl-S- <i>p</i> -tolyl-N-(N'-methylcarbamoyl)sulphoximine	95—98	Calculated for $C_{10}H_{14}N_2SO_2$ : C 53.2; H 6.2; N 12.4; S 14.2% Found : C 53.1; H 6.1; N 12.0; S 14.0%

TABLE 1 (Continued)

Compound	Melting Point °C.	Analysis
S-(3,5-dinitro-4-N',N'-dipropylaminophenyl)-S-methyl-N-propionylsulphoximine	173—175	Calculated for $C_{16}H_{24}N_4SO_6$ Found : C 48.0; H 6.0; N 14.0% : C 47.8; H 6.2; N 13.6%
S-(3,5-dinitro-4-N',N'-dipropylaminophenyl)-S-methyl-N-2,2-dichloropropionylsulphoximine	235—237	Calculated for $C_{16}H_{22}Cl_2N_4SO_6$ Found : C 40.9; H 4.7; N 11.9; S 6.8% : C 40.9; H 4.9; N 11.8; S 7.2%
S-(3,5-dinitro-4-N',N'-dipropylaminophenyl)-S-methyl-N-butyrylsulphoximine	163—165	Calculated for $C_{17}H_{26}N_4SO_6$ Found : C 49.3; H 6.3; N 13.5% : C 48.9; H 6.5; N 13.3%
S-(3,5-dinitro-4-N',N'-dipropylaminophenyl)-S-methyl-N-isobutyrylsulphoximine	206—209	Calculated for $C_{17}H_{26}N_4SO_6$ Found : C 49.3; H 6.3; N 13.5% : C 49.3; H 6.3; N 13.2%
S-(3,5-dinitro-4-N',N'-dipropylaminophenyl)-S-(methyl-N-benzoylsulphoximine	148—150	Calculated for $C_{20}H_{24}N_4SO_6$ Found : C 53.6; H 5.4; N 12.5% : C 53.6; H 5.5; N 12.4%
S-(3,5-dinitro-4-N'-propylaminophenyl)-S-methyl-N-acetylsulphoximine	102—104	Calculated for $C_{17}H_{24}N_4SO_6$ Found : C 41.9; H 4.7; N 16.3% : C 42.3; H 4.8; N 16.1%
S-(4-hydroxyphenyl)-S-methyl-N-tosylsulphoximine	186—188	Calculated for $C_{17}H_{18}NS_2O_4$ Found : C 51.7; H 4.7; N 4.3; S 19.7% : C 51.8; H 4.8; N 3.8; S 18.9%
S-(3,5-dinitro-4-N',N'-dipropylaminophenyl)-S-methyl-N-formylsulphoximine	133—135	Calculated for $C_{14}H_{20}N_4SO_6$ Found : C 45.2; H 5.4; N 15.1; S 8.6% : C 45.6; H 5.3; N 14.9; S 8.9%
S-(3-bromo-4-hydroxyphenyl)-S-methyl-N-tosylsulphoximine	178—180	Calculated for $C_{17}H_{14}NS_2O_4Br$ Found : C 41.6; H 3.5; N 3.5% : C 41.2; H 3.5; N 3.4%
S-(3,5-dibromo-4-hydroxyphenyl)-S-methyl-N-tosylsulphoximine	190—191	Calculated for $C_{14}H_{10}NS_2O_4Br_2$ Found : C 34.8; H 2.7; N 2.9% : C 34.4; H 2.7; N 2.8%
S-(4-chlorophenyl)-S-methyl-N-(N'-methylcarbamoyl)sulphoximine	141—143	Calculated for $C_{10}H_{11}N_2SO_2$ Found : C 43.7; H 4.5; N 11.3; S 12.9% : C 44.0; H 4.4; N 11.1; S 12.8%



TABLE 1 (Continued)

Compound	Melting Point °C.	Analysis
S-(3,5-dibromo-4-hydroxyphenyl)-S-methylsulphoximine	217—218	Calculated for $C_7H_7NSO_2Br_2$ : C 25.6; H 2.2; N 4.3; Br 48.6% Found : C 26.0; H 2.4; N 4.0; Br 48.9%
S-(3-bromo-4-hydroxyphenyl)-S-methylsulphoximinium sulphate	223—225	Calculated for $C_{14}H_{18}N_2O_8Br_2$ : C 28.0; H 3.0; N 4.7; S 16.0% Found : C 27.6; H 2.9; N 4.2; S 15.7%
S-(4-hydroxyphenyl)-S-methylsulphoximine	205—207	Calculated for $C_7H_9NSO_2$ : C 49.1; H 5.3; N 8.2; S 18.7% Found : C 49.4; H 5.4; N 7.8; S 18.3%
S-(4-diethoxyphosphinothioxyloxyphenyl)-S-methylsulphoximine	oil	Calculated for $C_{11}H_{18}PNS_2O_4$ : C 40.8; H 5.6; N 4.3; P 9.6% Found : C 41.7; H 5.9; N 4.9; P 9.1%
S-(4-diethoxyphosphinothioxyloxyphenyl)-S-methyl-N-tosylsulphoximine	75—77	Calculated for $C_{18}H_{24}PNS_2O_6$ : C 45.2; H 5.1; N 2.9; P 6.5% Found : C 44.8; H 5.2; N 2.7; P 6.4%
S-(4-hydroxy-3-iodophenyl)-S-methyl-N-tosylsulphoximine	172—175	Calculated for $C_{14}H_{14}NS_2O_4I$ : C 37.3; H 3.1; N 3.1% Found : C 36.5; H 3.1; N 2.8%
S-(3,5-diiodo-4-hydroxyphenyl)-S-methyl-N-tosylsulphoximine	204—206	Calculated for $C_{14}H_{13}NS_2O_4I_2$ : C 29.1; H 2.3; N 2.4% Found : C 30.0; H 2.4; N 2.2%
S-(3,5-diiodo-4-hydroxyphenyl)-S-methylsulphoximine	235—235 (dec.)	Calculated for $C_7H_7NSO_2I_2$ : C 19.9; H 1.7; N 3.3% Found : C 20.2; H 2.2; N 2.8%
S-(3,5-diiodo-4-hydroxyphenyl)-S-methylsulphoximine (Zwitterion)	215—217 (dec)	Calculated for $C_7H_7NSO_2I_2$ : C 19.9; H 1.7; N 3.3% Found : C 19.8; H 1.6; N 2.9%
S-(3,5-dinitro-4-N,N'-dipropylaminophenyl)-S-methyl-N-phenylsulphonylsulphoximine	163—165	Calculated for $C_{10}H_{24}N_4S_2O_7$ : C 47.1; H 5.0; N 13.2% Found : C 46.5; H 4.8; N 13.0%
N-(2,5-dinitro-4-methanesulphoximinophenyl)-N,N-dipropylammonium <i>p</i> -toluenesulphonate	115—118	Calculated for $C_{20}H_{28}N_4S_2O_8$ : C 46.4; H 5.5; N 10.8; S 12.4% Found : C 45.6; H 5.7; N 11.0; S 12.3%

## Example 10

## Herbicidal Activity

To evaluate their herbicidal activity, the compounds of the invention were tested using as a representative range of plants:—maize, *Zea mays* (Mz); oat, *Avena sativa* (O); rye grass, *Lolium perenne* (RG); pea, *Pisum sativum* (P); linseed, *Linum usitatissimum* (L); mustard, *Sinapis alba* (M); and sugar beet, *Beta vulgaris* (SB).

The tests fall into two categories, pre-emergence and post-emergence. The pre-emergence tests involved spraying a liquid formulation of the compound onto the soil in which the seeds of the plant species mentioned above had recently been sown. The post-emergence tests involved two types of test, viz. soil drench and foliar spray tests. In the soil drench tests the soil in which seedling plants of the above species were growing, was drenched with a liquid formulation containing a compound of the invention, and in the foliar spray tests the seedling plants were sprayed with such a formulation.

The soil used in the tests was a steam-sterilised, modified John Innes Compost mixture in which half the peat, by loose bulk, had been replaced by vermiculite.

The formulations used in the tests were prepared by diluting with water and solutions of the compounds in acetone containing 0.4% by weight of an alkylphenol/ethylene oxide condensate available under the trade name Triton (registered Trade Mark) X-155. In the soil

spray and foliar spray tests the acetone solutions were diluted with an equal volume of water and the resulting formulations applied at two dosage levels corresponding to 10 and 1 kilograms of active material per hectare respectively in a volume equivalent to 400 litres per hectare. In the soil drench tests one volume of the acetone solution was diluted to 155 volumes with water and the resulting formulation applied at one dosage level equivalent to 10 kilograms of active material per hectare in a volume equivalent to approximately 3,000 litres per hectare.

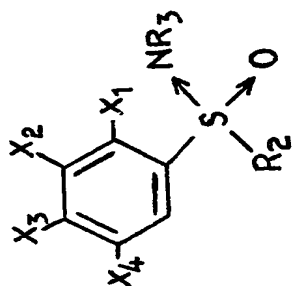
In the pre-emergence tests untreated sown soil and in the post-emergence tests untreated soil bearing seedling plants were used as controls.

The herbicidal effects of the compounds were assessed visually seven days after spraying the foliage and drenching the soil and eleven days after spraying the soil, and were recorded on a 0—9 scale. A rating 0 indicates no effect on the treated plants, a rating 2 indicates a reduction in fresh weight of stem and leaf of the plants of approximately 25%, a rating 5 indicates a reduction of approximately 55%, a rating 9 indicates a reduction of 95% etc.

The results of the tests are set out in Table 2.

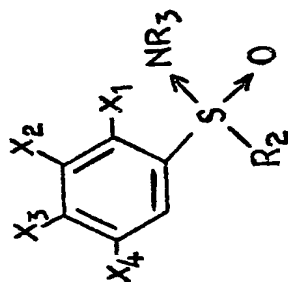
In the tests on certain of the compounds oat was replaced by rice, *Oryza sativa* (R) and rye grass was replaced by barnyard grass, *Echinochloa crusgalli* (BG). The results of these tests are given in Table 3.

TABLE 2



Compound						Dosage Kg/ha	Post-Emergence (Plants)												Pre-Emergence											
							Soil Drench						Foliar Spray						Soil Spray											
X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	X <sub>4</sub>	R <sub>3</sub>	R <sub>2</sub>	Mz	O	R	G	P	L	M	SB	Mz	O	R	G	P	L	M	SB	Mz	O	R	G	P	L	M	SB	
H	H	H	H	H	C <sub>6</sub> H <sub>5</sub>	H	10	1	0	0	3	2	0	0	2	1	1	7	6	6	0	1	0	0	0	0	0	0	0	0
H	H	NO <sub>2</sub>	H	CH <sub>3</sub>	H	CH <sub>3</sub>	10	1	0	2	5	0	0	3	4	1	3	7	1	4	9	9	0	0	1	0	0	4	0	
H	H	Cl	H	CH <sub>3</sub>	COCH <sub>3</sub>	CH <sub>3</sub>	10	1	0	0	0	0	0	0	0	0	2	1	1	7	6	3	0	0	0	0	0	0	0	
H	H	CH <sub>3</sub>	H	CH <sub>3</sub>	H	CH <sub>3</sub>	10	1	0	0	0	0	0	0	0	1	1	1	2	8	8	6	0	0	0	0	0	0	0	
H	H	NO <sub>2</sub>	HC	H <sub>3</sub>	COCH <sub>3</sub>	CH <sub>3</sub>	10	1	0	0	2	0	0	1	0	0	6	4	1	8	9	7	0	0	0	0	0	1	0	
Cl	H	NO <sub>2</sub>	H	CH <sub>3</sub>	H	CH <sub>3</sub>	10	1	0	0	0	0	0	0	0	3	6	6	8	9	9	9	0	0	0	0	0	0	0	
Cl	H	NO <sub>2</sub>	H	CH <sub>3</sub>	COCH <sub>3</sub>	CH <sub>3</sub>	10	1	0	0	0	0	0	0	0	1	3	1	2	7	9	4	0	0	0	0	0	0	0	
NO <sub>2</sub>	H	Cl	H	CH <sub>3</sub>	H	CH <sub>3</sub>	10	1	6	0	3	0	0	0	0	8	7	8	3	9	9	9	6	0	7	0	3	7	1	
H	H	Cl	H	CH <sub>3</sub>	H	CH <sub>3</sub>	10	1	0	1	0	0	1	0	0	0	1	1	4	4	8	6	0	1	0	0	0	0	0	

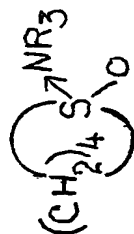
TABLE 3

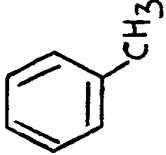


Compound						Dosage Kg/ha	Post-Emergence (Plants)										Pre-Emergence (seeds)													
							Soil Drench					Foliar Spray					Soil Spray													
X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	X <sub>4</sub>	R <sub>2</sub>	R <sub>3</sub>		Mz	R	B	G	P	L	M	SB	Mz	R	B	G	P	L	M	SB	Mz	R	B	G	P	L	M	SB
H	NO <sub>2</sub>	N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	NO <sub>2</sub>	CH <sub>3</sub>	H	10	7	5	7	0	0	0	0	0	8	7	8	5	7	8	5	0	3	6	9	0	5	7	8	5
NO <sub>2</sub>	H	H	H	CH <sub>3</sub>	H	10	5	4	8	1	8	8	6	6	7	8	9	4	9	9	9	7	8	9	9	1	6	8	6	
H	H	NO <sub>2</sub>	H	CH <sub>3</sub>	Cl	10	0	0	3	0	0	2	0	0	2	4	8	1	8	9	8	1	0	6	6	0	0	6	2	0
H	NO <sub>2</sub>	Cl	H	CH <sub>3</sub>	H	10	0	0	0	0	0	0	0	0	2	6	8	1	5	9	5	0	0	0	0	0	0	0	0	0
H	H	NO <sub>2</sub>	H	CH <sub>3</sub>	CON(CH <sub>3</sub> ) <sub>2</sub>	10	0	0	5	—	0	0	0	0	1	2	8	—	9	9	7	0	0	3	2	6	4	2	0	0
H	H	Cl	H	CH <sub>3</sub>	OCOC <sub>2</sub> H <sub>5</sub>	10	1	0	1	0	0	0	1	1	0	3	6	2	6	5	4	0	0	1	0	0	0	0	0	0
H	H	NO <sub>2</sub>	H	CH <sub>3</sub>	CONHC <sub>2</sub> H <sub>5</sub>	10	0	0	0	0	0	0	0	0	1	2	8	0	4	9	2	0	0	0	0	0	2	0	0	0

TABLE 3 (Continued)

Compound						Dosage Kg/ha	Post-Emergence (Plants)										Pre-Emergence (Seeds)														
							Soil Drench					Foliar Spray					Soil Spray														
X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	X <sub>4</sub>	R <sub>1</sub>	R <sub>2</sub>		Mz	R	B	G	P	L	M	SB	Mz	R	B	G	P	L	M	SB	Mz	R	B	G	P	L	M	SB	
H	NO <sub>2</sub>	NHC <sub>3</sub> H <sub>7</sub>	NO <sub>2</sub>	CH <sub>3</sub>	H	10 1	1	6	6	0	1	6	0		1	0	6	1	9	8	2	2	8	9	0	0	4	2	0	0	0
H	NO <sub>2</sub>	N(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	NO <sub>2</sub>	CH <sub>3</sub>	COCH <sub>3</sub>	10 1	7	6	6	0	0	0	0		6	4	5	0	3	3	0	7	9	9	0	0	2	4	1	1	
H	NO <sub>2</sub>	N(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	NO <sub>2</sub>	CH <sub>3</sub>	CONHCH <sub>3</sub>	10 1	3	5	4	0	0	0	0		1	3	2	0	1	3	0	6	9	9	0	0	3	7	0	0	
H	NO <sub>2</sub>	N(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	NO <sub>2</sub>	CH <sub>3</sub>	COCH <sub>2</sub> Cl	10 1	1	4	2	0	0	0	0		0	2	1	0	0	0	0	2	8	9	1	0	0	7	0	0	
H	NO <sub>2</sub>	N(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	NO <sub>2</sub>	CH <sub>3</sub>	COcyclo-propyl	10 1	6	5	3	0	0	0	0		0	1	0	0	3	2	0	1	8	9	0	0	0	5	0	0	
H	NO <sub>2</sub>	N(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	NO <sub>2</sub>	CH <sub>3</sub>	COC <sub>2</sub> H <sub>5</sub>	10 1	6	5	4	0	0	0	0		2	1	2	0	0	0	0	2	8	9	0	0	1	7	0	0	
H	NO <sub>2</sub>	NHC <sub>3</sub> H <sub>7</sub>	NO <sub>2</sub>	CH <sub>3</sub>	COCH <sub>3</sub>	10 1	1	3	3	0	1	8	0		0	0	2	0	6	7	2	5	8	9	0	0	2	4	0	0	
H	NO <sub>2</sub>	N(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	NO <sub>2</sub>	CH <sub>3</sub>	COH	10 1	6	5	6	0	0	0	2		3	4	5	0	4	4	1	8	9	9	0	4	5	9	1	6	
H	Br	OH	Br	CH <sub>3</sub>	H	10 1	—	—	—	—	—	—	—		0	2	4	0	7	9	9	4	9	2	0	8	6	7	0	0	
H	NO <sub>2</sub>	N(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	NO <sub>2</sub>	CH <sub>3</sub>	H	10 1	—	—	—	—	—	—	—		4	5	8	1	7	8	1	8	8	9	0	7	3	7	0	0	



Compound	Dosage Kg/ha	Post-Emergence (Plants)						Pre-Emergence (Seeds)						
		Soil Drench			Foliar Spray			Soil Spray						
		Mz	R	BG	P	L	M	SB	Mz	R	BG	P	L	M
	10	0	0	0	1	3	6	5						
	1	0	0	0	2	4	7	7						
COOCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	10	0	0	0	1	1	1	0						
	1	—	—	—	0	0	0	0						

### Example 11

### Insecticidal and Acaricidal Activity

**5** The insecticidal and acaricidal activity of the compounds of the invention was tested as follows:—

I. A 1.0% by weight solution in acetone of the compound to be tested was prepared, and taken up in a micrometer syringe. Two to three-day old adult female house flies (*Musca domestica*) were anaesthetized with carbon dioxide, and a 1  $\mu$ l drop of the test solution was brushed off

on the ventral abdomen of each, 20 flies being treated. The treated flies were held for 24 hours in glass jars, each containing a little

granulated sugar as food for the flies, and the percentages of dead and moribund individuals was then recorded.

II. A quantity of 0.1 ml of a 1.0% by weight solution of the compound to be tested in acetone was mixed in a beaker with 100 ml of water. Twenty 5—6 day-old (4th instar) mosquito larvae (*Aedes aegypti*) were added and the beakers stored for 24 hours. The percentage of dead and moribund larvae was then recorded.

III. The compounds were formulated as solutions or suspensions in water containing 20% by weight of acetone and 0.05% by weight of

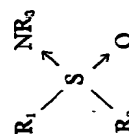
- 5 Triton X 100 as wetting agent. The formulations contained 0.7% by weight of the compound to be tested. Turnip and broad bean plants, trimmed to one leaf each, were sprayed on the under surface of the leaf with the above formulation. Spraying was effected with a spraying machine delivering 40 gallons per acre, the plants passing under the spray on a moving belt. Ten 4th instar (8-day-old) diamond-back moth larvae (*Plutella maculipennis*) or ten adult 1—2 week-old mustard beetles (*phaedon cochleariae*) were placed on the sprayed leaf of each turnip plant and ten apterous (6-day-old) vetch aphids (*Megoura viciae*) were placed on the sprayed leaf of each broad bean plant. The plants were then enclosed in glass cylinders fitted at one end with a muslin cap. Mortality counts were made after 24 hours.
- 10 IV. In tests against glass house spider mites (*Tetranychus urticae*), leaf discs cut from French bean plants were sprayed in the manner described under III. 1 hour after spraying, the discs were inoculated with 10 adult mites. Mortality counts were made 24 hours after inoculation.
- 15 V. In tests against large white butterfly larvae (*Pieris brassicae*), leaf discs cut from cabbage leaves were sprayed in the manner described under III. 103rd instar (8—10 day-old) larvae were placed on the discs within petri-dish pairs. Mortality counts were made 24 hours after inoculation.
- 20 The results of these tests are shown in Table 5 in which A denotes complete kill, B some kill and C no kill of the test insects.
- 25
- 30
- 35

TABLE 5

Compound	M. domestica	A. aegypti	P. cochleariae	P. maculipennis	P. brassicae	M. viciae	T. urticae
S,S-tetramethylene-N-(N'-m-tolyl-carbamoyl) Sulphoximine	A	C	C	C	—	C	B
S,S-tetramethylene-N-(benzyloxy-carbonyl) sulphoximine	A	B	C	C	—	C	A
S-(3,5-dibromo-4-hydroxyphenyl)-S-methyl-N-tosylsulphoximine	C	C	C	C	—	A	C
S-(3,5-dibromo-4-hydroxyphenyl)-S-methylsulphoximine	C	C	C	C	—	A	C
S-(4-diethoxyphosphinothioxyloxyphenyl)-S-methylsulphoximine	A	A	A	B	A	A	A
S-(4-diethoxyphosphinothioxyloxyphenyl)-S-methyl-N-tosylsulphoximine	C	C	A	A	A	A	A
S,S-diphenylsulphoximine	C	C	C	C	—	B	A

WHAT WE CLAIM IS:—

1. Biologically active compositions comprising a carrier or a surface-active agent, or both a carrier and a surface-active agent, together with as active ingredient a sulphoximine derivative of general formula:—



wherein R<sub>1</sub> represents an optionally substituted aryl group; R<sub>2</sub> represents an alkyl or aryl group, or R<sub>1</sub> and R<sub>2</sub> together represent a polymethylene group; and R<sub>3</sub> represents a hydrogen or halogen atom or a nitro or acyl group, or a salt of such a derivative.

2. Compositions as claimed in claim 1 in which the active ingredient is a sulphoximine derivative of formula I wherein R<sub>1</sub> represents a phenyl group optionally substituted by one or more halogen atoms, by one or more nitro groups, or by a hydroxy, alkyl, alkylamino, di-

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alkylamino or dialkylphosphorothionate group;  $R_2$  represents an alkyl group of 1—6 carbon atoms or a phenyl group, or  $R_1$  and  $R_2$  together represent a polymethylene group of up to 5 carbon atoms; and  $R_3$  represents a hydrogen or chlorine atom, a nitro group, an optionally chlorinated alkanoyl group of 1—6 carbon atoms, a cycloalkyl carbonyl group of up to 6 carbon atoms, an aroyl group, an N - substituted or N,N - disubstituted carbamoyl group, an alkoxy-carbonyl group, an aralkoxy-carbonyl group, an (alkylthio) carbonyl group or an alkyl-, aryl- or alkarylsulphonyl group, or a sulphate or alkarylsulphonate of such a derivative.

3. Compositions as claimed in claim 2 in which the active ingredient is a sulfoximine derivative of formula I wherein  $R_1$  represents a phenyl group optionally substituted by one or more chlorine, bromine or iodine atoms, by one or more nitro groups or by a hydroxy, methyl, propylamino, dipropylamino or diethylphosphorothionate group;  $R_2$  represents a methyl or phenyl group, or  $R_1$  and  $R_2$  together represent a tetramethylene group; and  $R_3$  represents a hydrogen or chlorine atom or a nitro, formyl, acetyl, chloroacetyl, dichloroacetyl, trichloroacetyl, propionyl, dichloropropionyl, butyryl, isobutyryl, cyclopropylcarbonyl, benzoyl, methylcarbamoyl, ethylcarbamoyl, phenylcarbamoyl, chlorophenylcarbamoyl, dichlorophenylcarbamoyl, tolylcarbamoyl, dimethylcarbamoyl, ethoxycarbonyl, benzyloxycarbonyl, (ethylthio) carbonyl, methylsulphonyl, phenylsulphonyl or tosyl group, or a sulphate or toluenesulphonate of such a derivative.

4. Compositions as claimed in claim 3 in which the active ingredient is a sulfoximine derivative of formula I wherein  $R_1$  represents a phenyl group optionally substituted by one or more chlorine atoms, by one or more nitro groups or by a methyl or dipropylamino group;  $R_2$  represents a methyl or phenyl group; and  $R_3$  represents a hydrogen or chlorine atom or a nitro, acetyl, methylcarbamoyl, ethylcarbamoyl, phenylcarbamoyl, chlorophenylcarbamoyl, dichlorophenylcarbamoyl, dimethylcarbamoyl, ethoxycarbonyl or (ethylthio) carbonyl group.

5. Compositions as claimed in claim 1 wherein the active ingredient is S - (3,5 - dinitro - 4 - N',N' - dipropylaminophenyl) - S - methylsulphoximine.

6. Compositions as claimed in any one of the claims 1—5 when formulated as powders, dusts, granules, solutions, emulsifiable concentrates, emulsions, suspension concentrates or aerosols.

7. Compositions as claimed in any one of the claims 1—6 substantially as hereinbefore described.

8. Sulfoximine derivatives of formula I wherein  $R_1$ ,  $R_2$  and  $R_3$  are as defined in claim 1, together with the salts thereof, with the pro-

viso that when  $R_1$  and  $R_2$  each represents a phenyl group or together represent a tetramethylene group, or  $R_1$  represents a phenyl group substituted in the 4-position by chloro, nitro or methyl and  $R_2$  represents a methyl group, then  $R_3$  is other than a hydrogen atom.

9. Sulfoximine derivatives as claimed in claim 8 wherein  $R_1$  represents a phenyl group optionally substituted by one or more halogen atoms, by one or more nitro groups, or by a hydroxy, alkyl, alkylamino, dialkylamino or dialkylphosphorothionate group;  $R_2$  represents an alkyl group of 1—6 carbon atoms or a phenyl group, or  $R_1$  and  $R_2$  together represent a polymethylene group of up to 5 carbon atoms; and  $R_3$  represents a hydrogen or chlorine atom, a nitro group, an optionally chlorinated alkanoyl group of 1—6 carbon atoms, a cycloalkyl carbonyl group of up to 6 carbon atoms, an aroyl group, an N - substituted or N,N - disubstituted carbamoyl group, an alkoxy-carbonyl group, an aralkoxy-carbonyl group, an (alkylthio) carbonyl group or an alkyl-, aryl- or alkarylsulphonyl group, or a sulphate or alkaryl sulphonate of such a derivative.

10. Sulfoximine derivatives as claimed in claim 9 wherein  $R_1$  represents a phenyl group optionally substituted by one or more chlorine, bromine or iodine atoms, by one or more nitro groups or by a hydroxy, methyl, propylamino, dipropylamino or diethylphosphorothionate group;  $R_2$  represents a methyl or phenyl group, or  $R_1$  and  $R_2$  together represent a tetramethylene group; and  $R_3$  represents a hydrogen or chlorine atom or a nitro, formyl, acetyl, chloroacetyl, dichloroacetyl, trichloroacetyl, propionyl, dichloropropionyl, butyryl, isobutyryl, cyclopropylcarbonyl, benzoyl, methylcarbamoyl, ethylcarbamoyl, phenylcarbamoyl, chlorophenylcarbamoyl, dichlorophenylcarbamoyl, tolylcarbamoyl, dimethylcarbamoyl, ethoxycarbonyl, benzyloxycarbonyl, (ethylthio) carbonyl, methylsulphonyl, phenylsulphonyl or tosyl group, or a sulphate or toluene sulphonate of such a derivative.

11. Sulfoximine derivatives as claimed in claim 10 wherein  $R_1$  represents a phenyl group optionally substituted by one or more chlorine atoms, by one or more nitro groups or by a methyl or dipropylamino group;  $R_2$  represents a methyl or phenyl group; and  $R_3$  represents a hydrogen or chlorine atom or a nitro, acetyl, methylcarbamoyl, ethylcarbamoyl, phenylcarbamoyl, chlorophenylcarbamoyl, dichlorophenylcarbamoyl, tolylcarbamoyl, dimethylcarbamoyl, ethoxycarbonyl, benzyloxycarbonyl or (ethylthio) carbonyl group.

12. S - (3,5 - dinitro - 4 - N',N' - dipropylaminophenyl) - S - methylsulphoximine.

13. Sulfoximine derivatives as claimed in claim 8 specifically named herein excluding that claimed in claim 12.

14. Process for preparing sulfoximine derivatives as claimed in claim 8 wherein  $R_3$

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represents a hydrogen atom which comprises reacting a sulfoxide of formula:—



- with hydrazoic acid.
- 5 15. Process according to claim 14 in which the hydrazoic acid is generated *in situ* by the action of an acid on an alkali metal azide.
- 10 16. Process according to claim 15 in which the acid is sulphuric acid and the alkali metal azide is sodium azide.
17. Process according to any one of the claims 14—16 in which the reaction is carried out in an organic solvent.
- 15 18. Process according to claim 17 in which the solvent is chloroform.
19. Process for preparing sulfoximine derivatives as claimed in claim 8 wherein  $R_2$  represents an acyl group which comprises reacting the corresponding compound wherein  $R_2$  represents a hydrogen atom with an acyl halide.
- 20 20. Process according to claim 19 in which the acyl halide is an acyl chloride.
- 25 21. Process according to claim 19 or 20 in which the reaction is carried out in the presence of a hydrogen halide acceptor.
22. Process according to claim 21 in which the hydrogen halide acceptor is a tertiary amine.
- 30 23. Process according to claim 22 in which the tertiary amine is triethylamine or pyridine.
24. Process according to any one of the claims 19—23 in which the reaction is carried out in an inert organic solvent.

25. Process according to claim 24 in which the solvent is ether.

26. Process for preparing sulfoximine derivatives as claimed in claim 8 wherein  $R_2$  represents a halogen atom which comprises reacting the corresponding compound wherein  $R_2$  represents a hydrogen atom with a halogenating atom.

27. Process according to claim 26 in which the halogenating agent is the elemental halogen or an alkali metal hypohalite.

28. Process for preparing sulfoximine derivatives as claimed in claim 8 wherein  $R_2$  represents a nitro group which comprises nitrating the corresponding compound wherein  $R_2$  represents a hydrogen atom using a mixture of nitric acid and sulphuric acid.

29. Process according to any one of the claims 14, 19, 26 or 28 substantially as hereinbefore described with particular reference to examples 1, 3, 4, 6 and 8.

30. Sulfoximine derivatives as claimed in claim 8 when prepared by a process as claimed in any one of the claims 14—29.

31. Method of combating weeds and/or insects and/or acarids at a locus which comprises applying to the locus a biocidally effective amount of a sulfoximine derivative as claimed in any one of the claims 8—13 or 30 or a composition as claimed in any one of the claims 1—7.

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